CATALYTIC PROPERTIES OF ZSM-TYPE ZEOLITES FORMED UNDER DIFFERENT CONDITIONS IN REACTIONS OF CONVERSION OF PARAFFINIC AND AROMATIC HYDROCARBONS

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ABSTRACT

Research has been made to compare catalytic properties of H-ZSM-5 type zeolites, H-mordenite (SiO_2:Al_2O_3 = 9-100) and silicalite, in reactions of paraffinic and aromatic hydrocarbons in hydrogen media at P = 3.5 MPa and T = 533-613 K. The H-ZSM-zeolite possesses much higher destruction activity in n-hexane conversion at much lower product isomerization degree which is noticed also with corresponding platinum catalysts. The difference between H-ZSM-zeolites and H-mordenites consists in the different qualitative composition of alkyl benzenes formed by the reaction between n-hexane and benzene. The results demonstrate the variety in chemical nature of n-hexane conversion over the tested zeolites.

INTRODUCTION

On the basis of the previously published data, it might be assumed that zeolites ZSM-5 could be synthesized only in the presence of quaternary ammonium bases or their derivatives. Later it became known that ZSM-5 zeolites might be easily cristallized from aluminosilicate mixtures either containing other organic compounds or without them. It might be expected that the usage of different organic compounds would lead to the formation of ZSM-5-type zeolites distinguished not only by their constitution, but also by their catalytic properties.

EXPERIMENTAL

In the present work, in order to investigate catalytic properties of ZSM-5 zeolites, the samples with various SiO_2:Al_2O_3 ratios

were synthesized. In order to eliminate the possible influence of organic compounds, butyl alcohol was used as organic component in all cases.

Silicalite was also synthesized in the silicate system in the presence of tetrapropylammonium hydroxide.

In all cases, the synthesis was conducted at 423 K in steel autoclaves with teflone inserts. The analytical data on the composition of initial mixtures and crystals are shown in Table 1.

Table 1

Chemical composition of initial mixtures and crystals of ZSM samples

Samples	Moles per 1 mole Al_2O_3					
	Initial mixtures				Crystals[x)]	
	Na_2O	SiO_2	H_2O	C_4H_9OH	Na_2O	SiO_2
ZSM-5	1.28	20	512	34.7	0.87	17
ZSM-5	3.62	60	1453	98.4	0.99	49
ZSM-5	4.10	100	1652	86.2	1.00	97.1

[x)] Incineration losses are to be neglected.
The composition of silicalite crystals corresponds to 0.011 moles Na_2O per 1 mole SiO_2.

ZSM-5 zeolites containing organics are stable to temperatures up to 973-1073 K, their thermostability increases with the increase in SiO_2:Al_2O_3 ratio in crystals. By means of chemical modification of ZSM-5 crystals, their thermostability can be risen up to 1273-1373 K.

In the present work, the properties of pentasiles have been investigated in conditions of paraffin hydrocracking which goes through disproportionation stages resulting mainly in the formation of initial hydrocarbon with the minimum yield of destruction products (C_1-C_2). The similar conversion of n-hexane has been studied over the catalyst on the base of H-mordenite under hydrogen pressure and at the temperature of 593-623 K [1, p. 341;2].

The experiments with mordenites (H-M) were used in this work as reference standards. The sample with silicate modulus 13 (standard), and mordenite obtained by dealuminizing of the standard with a ratio SiO_2:Al_2O_3 = 59 were studied.

Zeolite powdered was formed together with γ-Al_2O_3 (3:1, mass.). The tests were conducted in an ordinary unit of flow-through type. The

amounts of catalyst from 1 to 8 cm^3 with particle size 0.1-0.2 cm were used. Test conditions are listed in notes to Tables 2, 3 and Figures 1-3.

RESULTS AND DISCUSSION

The most significant difference of H-ZSM zeolites as opposed to H-M consists in their much higher destructive activity in conversion of n-hexane at lower (compared with H-M) product isomerization degree (Table 2).

Although the optimum value of silicate modulus approaches 50, the above conclusion is practically true for entire interval of its values (except the low-active silicalite), and also with the changing of conversion degree (10-70%) according to the experimental conditions (T = 533-613 K, LHSV = 4-16 hrs^{-1}).

Table 2

Conversion of n-hexane over H-M- and H-ZSM-type zeolites[x)]

No.	Zeolite/SiO_2:Al_2O_3	Conv. of n-C_6, mass%	Selectivity, %				iso/n		
			C_3	ΣC_4	ΣC_5	ΣiC_6	C_4	C_5	C_6
1	H-M/13	16.5	13.1	13.5	10.5	62.9	2.3	2.8	0.1
2	H-M/59	23.1	7.1	18.7	14.2	59.7	3.4	3.7	0.2
3	H-ZSM/17	33.4	19.8	39.8	25.2	15.2	0.7	0.8	0.1
4	H-ZSM/49	50.6	16.0	40.8	28.1	15.1	0.8	0.9	0.1
5	H-ZSM/100	37.3	15.9	40.3	28.2	15.6	0.8	0.9	0.1
6	Silicalite/~40 000	0.5	6.4	17.0	12.8	63.8	3.0	4.0	0.01

x) T = 573 K, LHSV = 8 hrs^{-1}, P_{H_2} = 3.5 MPa

The increase in conversion degree as a function of modulus (in the interval of 9-49) when passing from mordenite to ZSM is observed for corresponding platinum catalyst with the difference that platinum favours the formation of iso-hexane (in accordance with data [3]) with maximum selectivity for SiO_2:Al_2O_3 = 13 (Pt/H-M, Fig. 1).

The data on the comparison of catalitic activity between H-ZSM- and H-M-type zeolites support the conclusion [4,5] that the decline in number of acidic centers due to decrease in aluminium concentration is followed by the increase in their acidic strength. In the publications, this problem still remains controversial [4-7].

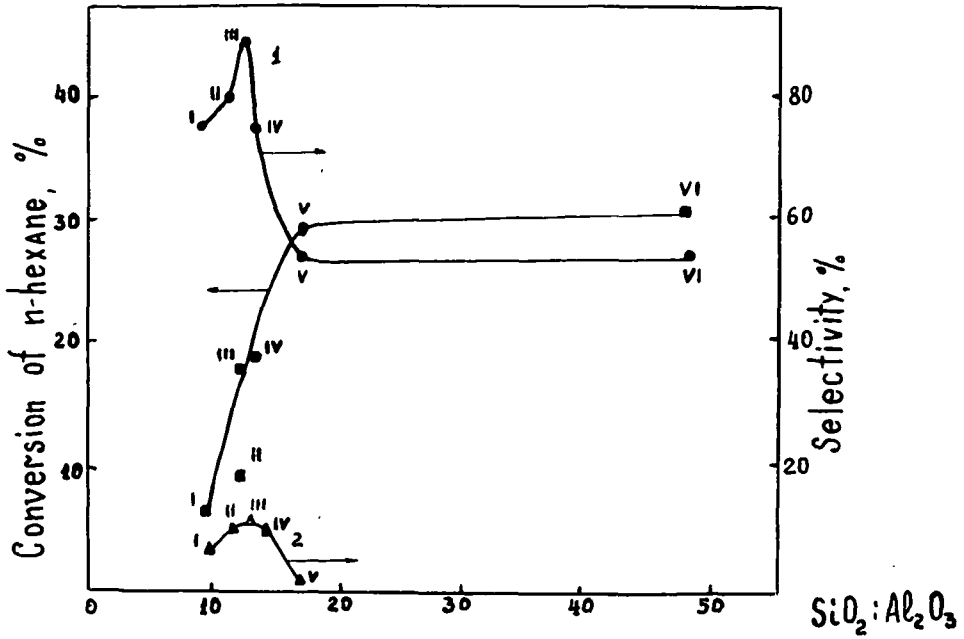


Fig. 1. Conversion of n-hexane over Pt/H-M and Pt/H-ZSM
1 - Selectivity of iso-C_6 formation
2 - Selectivity of 2,2-dimethylbutane formation
I-IV - Pt/H-M
V-VI - Pt/H-ZSM

We have previously shown that, when n-hexane destruction products react with benzene over dealuminized H-M, the main initial product is ethylbenzene [8]. The similar product distribution is observed over standard H-M with modulus equal to 13 (Fig. 2, 1-2).

The zeolites of H-ZSM-type are at the similar conditions characterized by the formation of mainly propylbenzenes along with the formation of higher alkylbenzenes and minimum quantities of ethylbenzene irrespective to conversion degree and silicate modulus (Fig. 2, 3-5).

The conversion of benzene without paraffin at these conditions is negligible, so the composition of alkylbenzenes (if secondary reactions are restricted) depicts the composition of n-hexane distribution products, which are intermediates in the formation of final products, paraffins C_3-C_5. Thus, the prevalence of propylbenzenes over H-ZSM shows the significant difference in chemical mechanisms on n-hexane destruction over H-ZSM and over H-M at the same conditions.

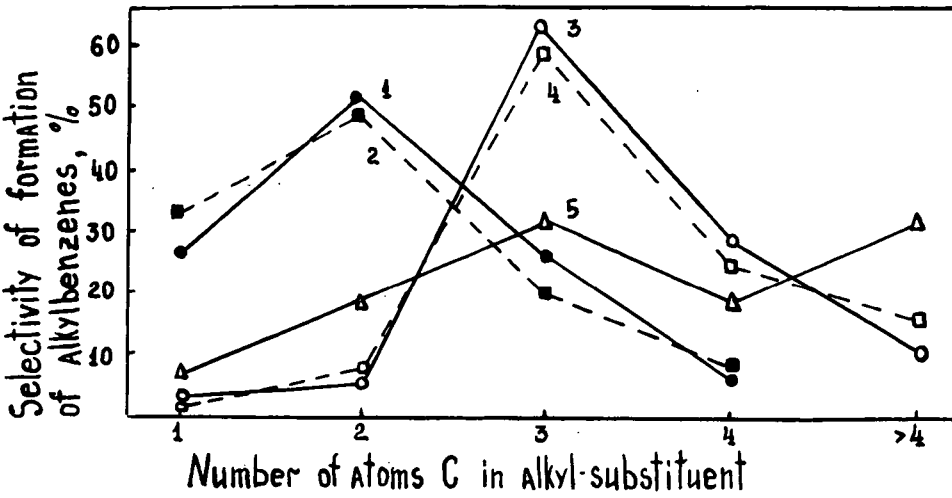
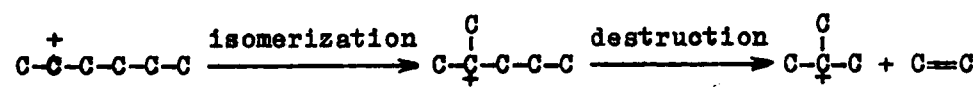


Fig. 2. Distribution of alkylbenzenes in the product of reaction between n-hexane and benzene (86 mole % $n\text{-}C_6H_{14}$ + 14 mole % C_6H_6) over zeolites of H-ZSM- and H-M-type

	$SiO_2:Al_2O_3$	T, K	LHSV, hrs^{-1}	$n\text{-}C_6H_{14}$ conversion, mass %	C_6H_6 conversion, mass %
1 - H-M	13	613	8	18.4	12.1
2 - H-M	59	613	8	28.0	15.0
3 - H-ZSM	17	533	16	20.0	19.4
4 - H-ZSM	49	533	16	22.0	21.7
5 - H-ZSM	17	613	4	70.0	67.2

This effect may be explained by means of the schemes listed below:

I (over H-M):



II (over H-ZSM):

It is supposed that the formation of branched structures on H-ZSM-zeolites compared to H-M faces difficulties due to the reduction of effective channel radii in the ZSM structure, which is evidenced by the suppression of 2,2-dimethylbutane formation. At the same time, strong acidic centers of H-ZSM catalyze cleavage with the formation of C_3 fragments (i.e. Scheme II prevails).

It should be noticed that introduction of small amounts of benzene (14%) into the hydrocarbon does not affect the conversion of n-hexane over H-ZSM. Only an excess of benzene (88%) causes some reaction retardation (Table 3).

Table 3

Conversion of n-hexane over zeolites of H-M- and ZSM-type in the presence of benzene[x)]

No.	Zeolite/SiO_2:Al_2O_3	Benzene alkylation degree, mass %	n-Hexane conversion, mass %	Selectivity, %			
				C_3	C_4	C_5	iC_6
	Feedstock: 86 mole% n-C_6H_{14} + 14 mole% C_6H_6						
1	H-M/13	3.8	10.5	10.4	15.4	10.5	63.7
2	H-M/59	6.0	14.6	6.9	13.4	9.2	70.5
3	H-ZSM/17	36.3	34.9	17.4	37.5	25.7	19.4
4	H-ZSM/49	67.5	53.6	15.3	41.1	28.7	14.9
	Feedstock: 12 mole% n-C_6H_{14} + 88 mole% C_6H_6						
5	H-ZSM/17	1.5	29.3	15.4	28.2	22.2	34.2

x) T = 573 K, LHSV = 8 hrs^{-1}

The formation of higher alkylbenzenes is the result of benzene alkylation by the products of oligomerization that also observed in the reaction of benzene alkylation by ethylene on acidic catalysts [1, p. 392].

Actually, in the experiments with mixture containing excess of benzene, there was observed an abrupt decrease in higher alkylbenzen yield with the formation of equal amount of ethylbenzene (Fig. 3).

Therefore, the presence of ethyl- and butylbenzenes in the primary products formed over H-ZSM points to the fact that n-hexane conversion in this case partially follows Scheme (I).

The fact, that ethylene oligomerization at relatively low benzene concentration (12% compared to 88% over H-ZSM) is prevented over H-M, agrees well with the above conclusion that H-ZSM-type zeolites have acidic centers with higher strength.

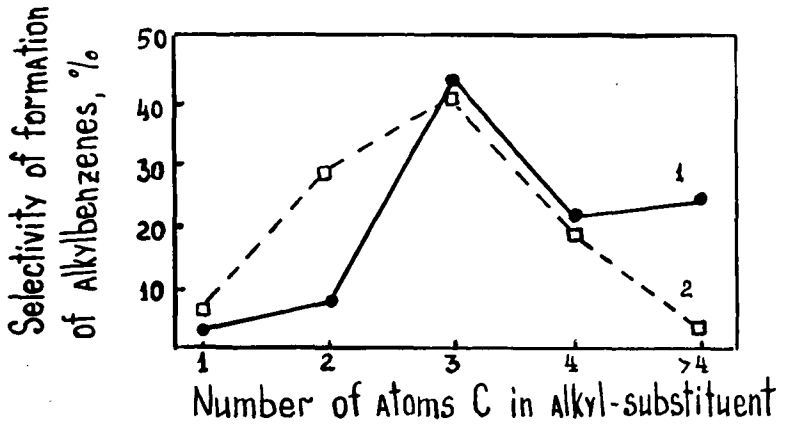


Fig. 3. The effect of bezene concentration on the distribution of alkylbenzenes over H-ZSM zeolite
$SiO_2:Al_2O_3$ = 17, T = 573 K, LHSV = 8 hrs^{-1}
1 - 14 mole % C_6H_6, 2 - 88 mole % C_6H_6

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